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The Persistence of Parathion, Toxaphene, and Methoxychlor in Soil

By CALEB PAGAN CARLO, DONALD ASHDOWN, and V. G. HELLER*

WHENEVER A NEW CHEMICAL shows value as an insecticide, fungicide, herbicide or for other agricultural use, it becomes important to know whether it is toxic to plants, either when applied to the plant or when incorporated into the soil, and also to know whether it persists in the soil, is broken down chemically by organisms, or is leached from the soil. Experiments described in this bulletin sought to obtain information on the persistence in soil of the new insecticides, parathion (O, O-diethyl-O-paranitrophenylthiophosphate), toxaphene (a mixture of chlorinated camphenes), and methoxychlor (2, 2 bis (p-methoxyphenyl) 1, 1, 1, trichloroethane).

The purpose of these investigations was three-fold:

(A) To obtain information as to the persistence of known amounts of parathion, toxaphene and methoxychlor when mixed with the soil.

(B) To study the effect of soil pH on the rate of decomposition of these compounds.

(C) In the case of parathion, to determine if volatilization is the main cause of the disappearance of this insecticide when mixed with soil.

Review of Literature

Studies on the decomposition and phytotoxicity of soil residues of the synthetic organic insecticides center almost exclusively on DDT (p, p' dichlorodiphenyltrichloroethane). Even in this case, there is

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some disagreement in the results obtained by different workers. Foster (7) reported that DDT mixed in muck soil and exposed to outdoor weathering remained stable and persisted without detectable changes in toxicity for a period of four years. Fleming (6) found that the effectiveness of DDT residues in some types of soils did not change in five years, but that in other soil types the toxicity decreased considerably. Sakimura (15) reported that the residual toxicity of DDT dropped by two-thirds after 26 months of application. It appears, therefore, that the decomposition of this insecticide in soil varies with different types of soil (3, 6, 8).

Parathion has been shown to be translocated throughout the plant when applied to the leaves in the form of spray. Likewise, it is absorbed through the roots of plants (3) and through the fruit (4); and some plants grown in treated soil produced tissue lethal to insects (10).

Parathion decomposes and rapidly loses its insecticidal activity, according to Ginsburg *et al.* (9). They found virtually no residues on crops harvested 12 or more days after application of the insecticide in dusts or sprays. Furthermore, parathion disappears rapidly when exposed on an inert glass surface. Among the possible explanations are volatilization, mechanical dissipation, and decomposition. The general consensus is that the disappearance of parathion residues is due predominantly to direct volatilization.

Zimmerman and Hartzell (20) postulate that organic phosphates in the soil decomposes to produce ethylene vapors, basing this hypothesis on their observations that plants grown in treated soil showed typical symptoms of ethylene poisoning. However, McIlrath (11) produced similar malformations in cotton plants by direct application of commercial formulations of parathion on the leaves, thus suggesting that the results observed by Zimmerman and Hartzell may have been due to absorption of parathion through the roots and its translocation to the leaves.

There is, therefore, some disagreement as to the stability of parathion residues and the possible causes of its deterioration.

Toxaphene is highly toxic to certain plants, but the toxicity of soil residues of this insecticide is a controversial subject in the literature. Cullinan (2) reports that toxaphene depressed plant growth when applied to the soil at low levels, whereas Watts (18) could detect no damage to cotton planted in soil containing the equivalent of 2,000 pounds toxaphene per acre. Woodbury (19) mentions that toxaphene deposits in soil may be transitory; on the other hand, Foster (7) reports that large amounts of toxaphene in the soil remain toxic to crops for several months.

Methoxychlor, in contrast to DDT, has less tendency to be stored in the body fat and to be excreted in the milk of treated animals (17).

All three of these insecticides are highly unstable in alkaline solutions. Presumably, they should be stable in mildly acid media; however, no specific statement to this effect has been found in the literature.

To our best knowledge, no work has been reported on the possible effects of soil pH on residues of parathion, toxaphene and methoxychlor. Research on this problem is important not only for these insecticides but with all chemicals applied to crops.

Materials and Methods

Three experiments were conducted, one with each insecticide. Each experiment included three soil treatments: A control of untreated soil, an acid soil, and a basic soil. Samples of the untreated soil showed a pH of 6.5. The soil used was a Stephenville fine sandy loam, rich in organic matter, which had never been previously sprayed or treated in any way for control of insects or weeds.

Individual 500-gram samples of soil were weighed into half-gallon glass jars. To prepare an alkaline soil, one gram of calcium hydroxide was added and completely mixed with the 500 grams of soil. A pH of 7.8 was thus obtained. One-half gram of aluminum sulfate added to 500 grams of the raw soil produced a pH of 4.7.

Each insecticide was diluted with water so as to give 100 milligrams of actual toxicant in a 20-milliliter aliquot. This was pipetted into each jar and thoroughly mixed with the soil. Five replicate sets of samples were prepared with each insecticide.

The prepared jars of soil were carried under greenhouse cover during the course of the experiments, so as to keep the soil at **comparable conditions** of **temperature** and **humidity.** The jars were kept open (except as noted below for parathion) and the soil moisture was maintained by daily additions of water. The jars were shaken periodically to expose a fresh portion of the soil to the air, in an attempt to simulate actual field conditions.

One of the five replicated samples was analyzed immediately to determine the recovery of the toxicant under the experimental conditions. The others were analyzed at the end of 1-, 2-, 4- and 8-week intervals thereafter.

In the case of parathion, duplicate sets of samples were prepared for each of the sampling intervals. In half of the series the jars were

sealed airtight to prevent possible volatilization of the insecticides; in the other half of the series the jars were left open.

At the time of analysis the soil samples were extracted with 600 milliliters of solvent in closed mason jars. Six jars at a time were tumbled end over end in a shaking machine at approximately 50 r.p.m. for 60 minutes. Benzene was used to extract parathion and methoxychlor, and a mixture of two parts benzene and one part of isopropanol was used for extracting toxaphene. The extract was filtered and a suitable aliquot measured into a breaker. The solvent was evaporated at low temperature under a current of air to reduce decomposition of the insecticide, and the dried residue was then analyzed.

Parathion was determined by the method developed by Averell and Norris (1) for analyzing spray residues. This method is based on reduction of the nitro group of parathion to the amine, diazotization and coupling with N-(1-naphthyl) ethylenediamine hydrochloride, which gives an intense magenta color with an absorption peak at 555 mu.

There is no specific qualitative or quantitative test for toxaphene. The total chlorine content of toxaphene was determined by refluxing the extract in isopropanol solution with metallic sodium. The chlorides liberated were then estimated by the titration method of McLean and Van Slyke (12).

Methoxychlor was determined by the method of Fairing and Warrington (5).

Results and Discussion

The results obtained in the experiments with parathion, toxaphene and methoxychlor are presented in Tables I, II, and III, respectively. Analyses of the soil immediately after mixing with the insecticide showed essentially complete recoveries of the amounts of parathion and toxaphene added, but only about 90 per cent of the added methoxychlor was recovered.

PARATHION.—The decomposition of parathion proceeded gradually but consistently, and at the end of 8 weeks only about one-third of the insecticide remained in the soil (Table I). The disintegration of the toxicant was most rapid during the first two weeks, when about 40 mg. was lost. The amount of parathion applied was much larger than would be expected to accumulate in the soil from spray run-off. It follows that there is little probability of "poisoning" the soil with parathion by normal usage for insect control, since its rate of decomposition is very high in the first few days after application.

TABLE I.—CONCENTRATIONS OF PARATHION RECOVERED FROM SOIL AT STATED INTERVALS AFTER APPLICATION.*

Time interval**	Acid (pH 4.7)		Untreated (pH 6.5)		Basic (pH 7.8)	
	Open	Closed	Open	Closed	Open	Closed
	mg.	mg.	mg.	mg.	mg.	mg.
1 Week	76.5	74.4	72.3	72.0	67.2	71.7
2 Weeks	55.2	62.0	65.6	61.4	43.0	45.6
4 Weeks	51.3	51.3	49.2	54.0	40.7	45.8
8 Weeks	35.2	35.9	34.8	35.5	27.9	27.3

* Averages of duplicate samples.

** Analysis in triplicate of the soil immediately after mixing with the insecticide showed a concentration of 104.5 mg. parathion.

There was no significant difference between the amounts of insecticide recovered from the closed and open jars, which suggests that the deterioration of parathion is mainly, if not entirely, a chemical process.

The stability of parathion, as measured by its recovery was similar in the acid soil and in the control. However, the alkaline soil definitely increased the rate of decomposition, the recovery of parathion from basic soil being around 20 to 30 percent less than from the acid or neutral soil.

TOXAPHENE.—The results obtained with toxaphene followed a somewhat different pattern (Table II). By the end of the first four weeks about 30 percent of the toxaphene was lost, presumably through decomposition. From then on, the residue remained practically constant through the last four weeks. Toxaphene is a mixture of chlorinated camphenes, and it may well be that some of the isomers are less stable than others, thus accounting for the initial decrease in the apparent concentration.

Liming of the soil had a pronounced effect on the stability of toxaphene residues. At the end of eight weeks about 50 percent of the insecticide had disappeared from the basic soil as compared to 30 percent for the acid and neutral soils. The relative stability of this insecticide in acid and near neutral soils may constitute a serious hazard, since toxaphene mixed with the soil at relatively high concentrations has been proposed for the control of the corn root worm and other soil pests (15, 20). The effect of liming in enchancing the rate of decomposition might

TABLE II.—CONCENTRATIONS OF TOXAPHENE RECOVERED FROM SOIL AT STATED INTERVALS AFTER APPLICATION.

Time interval*		Acid (pH 4.7)	Untreated (pH 6.5)	Basic (pH 7.8)
		mg.	mg.	mg.
1 Week	(a)	82.7	84.6	83.8
	(b)	80.8	82.8	85.1
	Av.	81.8	83.7	84.5
2 Weeks	(a)	73.1	80.4	80.4
	(b)	75.9	78.7	77.9
	Av.	74.5	79.5	79.2
4 Weeks	(a)	70.4	72.2	51.3
	(b)	72.6	66.4	53.0
	Av.	71.6	69.3	52.2
8 Weeks	(a)	70.3	69.3	48.3
	(b)	72.9	67.1	49.5
	Av.	71.6	68.2	48.9

* Analysis in triplicate of the soil immediately after mixing with the insecticide showed a concentration of 96.2 mg. chlorinated camphenes.

have some practical applications in decontaminating soils "poisoned" with this insecticide.

According to Smith and Wenzell (16), toxephene is attacked by the soil bacteria. They further postulate that the insecticide is a source of food for soil micro-organisms. The results presented by these workers are not too conclusive, since by their own admission adequate controls were not kept in their experiments. The data presented in Table II are not in entire agreement with the conclusions of Smith and Wenzell, and additional work along these lines would be highly desirable.

METHOXYCHLOR.—Contrary to all expectations, methoxychlor was the least stable of the three insecticides studied. Close to 75 percent of the insecticide deteriorated in the first two weeks. Like toxaphene, the remaining deposit of methoxychlor persisted relatively constant for the duration of the experiment. It is evident from the data that the chances of building up a toxic residue of this material in soil, through repeated spraying, are very small. Liming of the soil significantly accelerated the destruction of the insecticide.

Conclusions

Parathion, toxaphene and methoxychlor were mixed with soil of

TABLE III.—CONCENTRATIONS OF METHOXYCHLOR RECOVERED FROM SOIL AT STATED INTERVALS AFTER APPLICATION.

Time interval*		Acid (pH 4.7)	Untreated (pH 6.5)	Basic (pH 7.8)
		mg.	mg.	mg.
1 Week	(a)	48.3	53.7	40.0
	(b)	54.4	55.0	39.5
	Av.	51.4	54.4	39.8
2 Weeks	(a)	29.8	30.8	22.5
	(b)	31.8	34.3	24.3
	Av.	30.8	32.5	23.4
4 Weeks	(a)	27.3	27.5	15.3
	(b)	29.0	31.1	19.5
	Av.	28.2	29.3	17.4
8 Weeks	(a)	23.7	22.5	17.7
	(b)	23.1	23.7	16.6
	Av.	23.4	23.1	17.2

* Analysis in triplicate of the soil immediately after mixing with the insecticide showed a concentration of 89.6 mg. methoxychlor.

three pH levels. Analyses made at intervals of 1, 2, 4 and 8 weeks thereafter indicate the following conclusions:

(a) Toxaphene was the most persistent of the three insecticides studied, parathion was somewhat less stable, and methoxychlor the least permanent.

(b) The three insecticides showed rapid disappearance during the first two weeks after application; this limits the possibility of heavy buildup and a permanent poisoning of the soil by repeated spraying with these toxicants.

(c) Increasing soil pH by adding lime greatly accelerated the decomposition of the insecticides, the effect being most pronounced in the case of toxaphene.

(d) Parathion was not lost from the soil by volatilization to any appreciable extent; rather, the insecticide disappeared slowly, presumably by chemical degradation.

(e) In all cases, the insecticides were detected in the soil at the end of eight weeks; therefore, these chemicals should be used cautiously when applied at high concentration directly to the soil for the control of insects and other soil pests.

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